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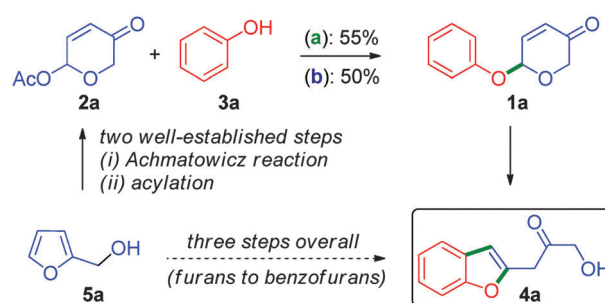
Synthesis of benzofurans *via* an acid catalysed transacetalisation/Fries-type O → C rearrangement/Michael addition/ring-opening aromatisation cascade of β-pyrone†

Siddheshwar K. Bankar, Jopaul Mathew and S. S. V. Ramasastry*

An unusual and facile approach for the synthesis of 2-benzofuranyl-3-hydroxyacetones from 6-acetoxy-β-pyrone and phenols is presented. The synthetic sequence involves a cascade transacetalisation, Fries-type O → C rearrangement followed by Michael addition and ring-opening aromatisation. The versatility of this method was further demonstrated *via* the synthesis of 4,4a-dihydropyrano[3,2-*b*]benzofuran-3-ones, furo[3,2-*c*]coumarins, and spiro[benzofuran-2,2'-furan]-4'-ones. The unexpected cascade event would also provide new possible considerations in the β-pyrone-involved organic synthesis.

Benzofurans are ubiquitous building blocks in many bioactive natural products and primary structural motifs in several pharmaceuticals and molecular electronics.¹ Furthermore, benzofurans are acclaimed privileged scaffolds in drug discovery.² These distinguished features stimulated the development of several efficient and concise strategies for the synthesis of diverse benzofuran derivatives.³ However, owing to the limitations of the conventional approaches, such as the harsh reaction conditions, broad substrate scope and limited functional-group tolerability, there still exists ample scope for exploring new approaches for the synthesis of benzofurans. Herein, we report a new access to benzofurans *via* a Lewis acid catalysed one-pot cascade process.

Development of novel cascade processes has received great attention owing to their exceptional ability to rapidly assemble intricate molecular scaffolds.⁴ As part of our recent efforts to develop new cascade approaches for the O,S-containing heterocycles, it necessitated us to have rapid and efficient access to 6-aryloxy-β-pyrone of the type **1a**.⁵ For this purpose, the Lewis acid catalysed protocols of Gryniewicz^{6a} and Feringa^{6b} were tried with 6-acetoxy-β-pyrone **2a** and phenol **3a**, but the required



(a) Gryniewicz conditions: SnCl₄, 1,2-dichloroethane, 0–5 °C, 10 min
(b) Feringa conditions: BF₃OEt₂, 1,2-dichloroethane, 0–5 °C, 5 min

Scheme 1 Unprecedented cascade reaction of 6-acetoxy-β-pyrone and phenols leading to the synthesis of 1-(2-benzofuranyl)-3-hydroxyacetones.

product **1a** was isolated in low yields, Scheme 1.⁷ A detailed investigation revealed that the formation of a polar compound (on TLC) was responsible for the yield loss. Further study of the reaction under Feringa's conditions revealed that the concentration of the initially formed phenyl ether **1a** started diminishing and simultaneous build-up of the unanticipated product **4a** was observed. Thus, we have drawn the conclusion at this stage that the unexpected product **4a** formed *via* the intermediacy of **1a**. The structure of the unexpected product **4a** was deduced from ¹H and ¹³C NMR data and was further confirmed by single-crystal X-ray diffraction analysis (*vide infra*).⁸ Since the 6-acetoxy-β-pyrone **2a** can be accessed from furyl carbinol **5a** in two straightforward steps,⁵ this protocol thus represents an unique three-step conversion of furans (of the type **5a**) to benzofurans (such as **4a**), Scheme 1.⁹

Having realised the significance of benzofurans especially generated under mild Lewis acidic conditions from readily accessible starting compounds, and considering the potential implications of this rearrangement in organic synthesis, we turned to optimising the reaction conditions. Towards this, various Lewis acid and solvent combinations were investigated, and few important results are shown in Table 1.

The reaction catalysed by La(OTf)₃ generated exclusively the 6-phenoxy-β-pyrone **1a** even after extended reaction times,

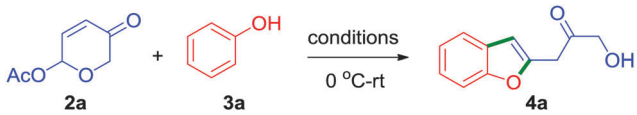
Organic Synthesis and Catalysis Lab, Department of Chemical Sciences,
Indian Institute of Science Education and Research (IISER) Mohali, Knowledge City,
Sector 81, S. A. S. Nagar, Manali PO, Punjab 140306, India.

E-mail: ramsastry@iisermohali.ac.in, ramsastry@gmail.com;

Web: <http://14.139.227.202/faculty/sastry/>

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Table 1 Optimisation of the reaction parameters^a


Entry	Acid (10 mol%)	Solvent	Time (h)	Yield ^b (%)
1	La(OTf) ₃	DCE	48	74 ^c
2	SnCl ₄	DCE	3	50
3	BF ₃ OEt ₂	DCE	18	55
4	FeCl ₃	DCE	18	45
5	In(OTf) ₃	DCE	20	48
6	Zn(OTf) ₃	DCE	20	45
7	Bi(OTf) ₃	DCE	20	61
8	AgOTf	DCE	21	40
9	TMSOTf	DCE	20	74
10 ^d	TMSOTf	DCE	20	47
11 ^{e,f}	TMSOTf	DCE	30	45
12 ^g	TMSOTf	DCE	72	—
13	TfOH	DCE	20	63
14	PTSA	DCE	20	51
15	TMSOTf	CH ₃ CN	21	48
16	TMSOTf	Toluene	72	25
17	TMSOTf	THF	72	—

^a A 5 mL glass vial was filled with **2a** (0.2 mmol), **3a** (0.22 mmol), and a solvent (1 mL). A catalyst (0.02 mmol) was then added at 0–5 °C. After stirring at the same temperature for about 30 min, the reaction continued at room temperature until **1a** and **2a** disappeared (by TLC).

^b Isolated yield after column chromatography. ^c **1a** exclusively formed.

^d 20 mol% TMSOTf was employed. ^e 5 mol% TMSOTf was employed.

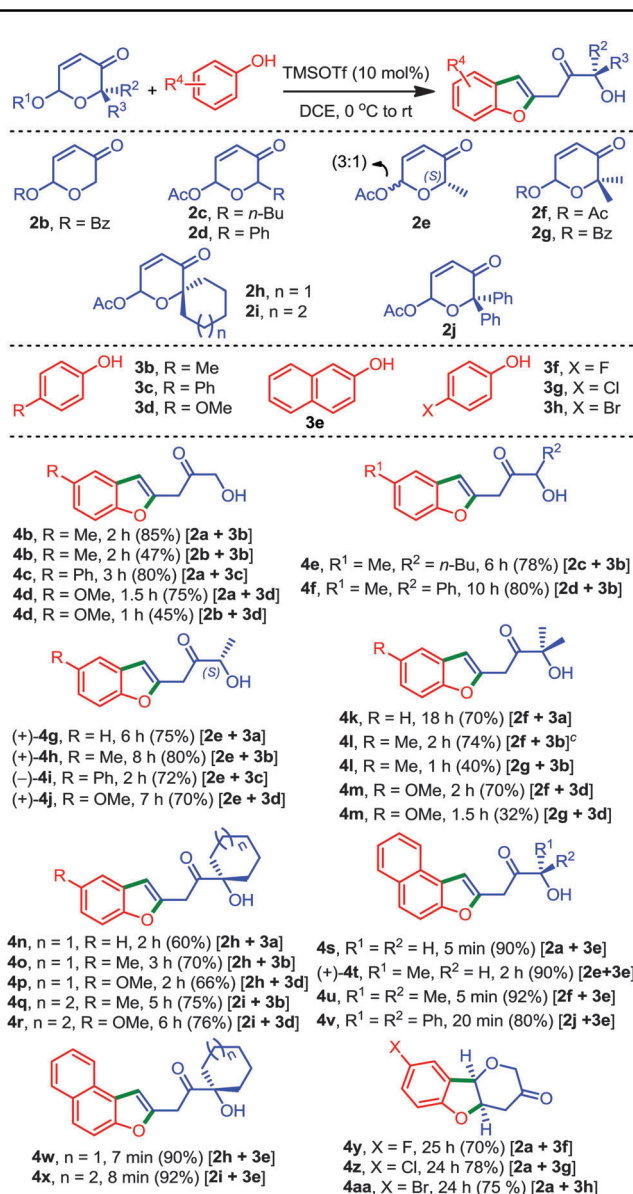
^f **1a** and **2a** were also recovered. ^g In the presence of 2,6-di-*tert*-butyl-4-methylpyridine (1 equiv.).

thereby establishing a high-yielding method for its selective synthesis (Table 1, entry 1). Most of the Lewis acids employed during the screening otherwise furnished the desired product **4a** in varied yields, with TMSOTf giving the best result (entries 2–9). Reaction with higher TMSOTf loading (20 mol%) gave a poor result due to the formation of undesired side products (entry 10). On the other hand, reaction in the presence of 5 mol% TMSOTf was found to be sluggish (entry 11). So, 10 mol% TMSOTf loading was realised to be optimal for this transformation.

Interestingly, the reaction in the presence of a proton sponge such as 2,6-di-*tert*-butyl-4-methylpyridine completely inhibited the product formation, indicating most likely that catalytic amounts of TfOH generated *in situ* might be promoting this process (entry 12). However, despite repeated attempts, TfOH furnished the required product in lower yields when compared to TMSOTf (entry 13). Among few other Brønsted acids employed, PTSA generated **4a** in satisfactory yield (entry 14). So, TMSOTf was identified as the catalyst of choice for this study considering its mild nature and ease of handling. Brief solvent screening with TMSOTf offered no further improvement in the yield (Table 1, entries 15–17).

With the optimised reaction conditions in hand, the scope of the reaction was subsequently investigated, and the representative results are presented in Table 2. Since the 6-benzoyloxy- β -pyrones (**2b** and **2g**) afforded the respective products (**4b**, **4d**, **4l**, and **4m**) consistently in low yields under the optimised conditions, acetates of β -pyrones were preferred over benzoates during this study.

A variety of 6-acetoxy- β -pyrones (**2c–2f**, **2h–2j**) and phenols (**3b–3e**) conveniently generated the respective benzofurans **4b–4x** in good to

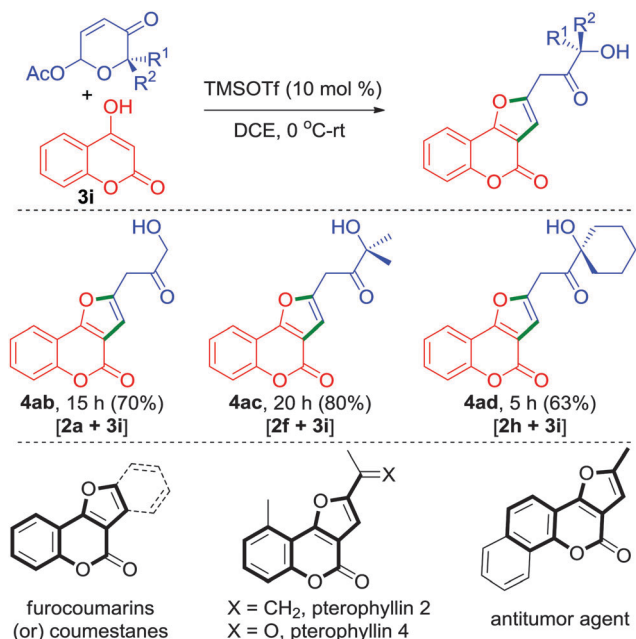
Table 2 Substrate scope^{a,b}

^a A 5 mL glass vial was filled with **2** (0.2 mmol), **3** (0.22 mmol), and DCE (1 mL). TMSOTf (0.02 mmol) was then introduced at 0–5 °C. After stirring at the same temperature for 30 min, the reaction continued at room temperature until **1** and **2** disappeared (by TLC). ^b Isolated yield after column chromatography. ^c Structure confirmed by single crystal X-ray diffraction analysis, see the ESI for details.¹⁰

excellent yields.¹¹ A range of possible substitution patterns on the pyrones were considered that provided 2-benzofuranyl propanones possessing 1°, 2° and 3°-alcoholic centres. Notably, chiral hydroxyacetones such as **4g–4j** and **4t** can be easily assembled by employing this strategy. In particular, isolation of alcohols **4j** and **4t** in 98% and 93% ee, respectively, indicates the involvement of a non-racemising process during the transformation which in turn signifies the mildness of the reaction conditions.

Interestingly, the reaction of the pyrone **2a** with halogenated phenols **3f–3h** generated only the 4,4a-dihydropyrano[3,2-*b*]-benzofurans **4y**, **4z**, and **4aa**. Even prolonged reaction times



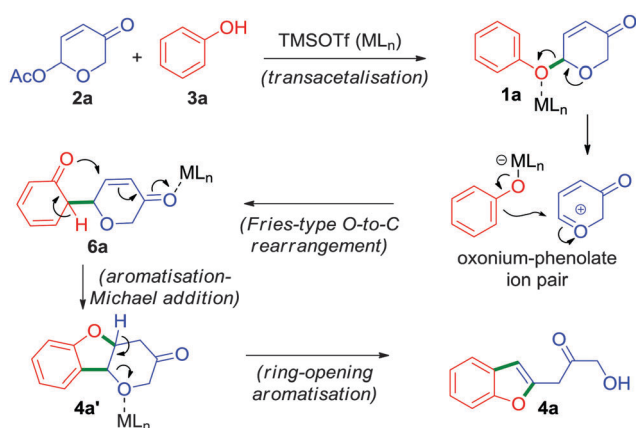


Scheme 2 Unprecedented approach for the synthesis of furo[3,2-*c*]coumarins and a few representative bioactive furocoumarins.

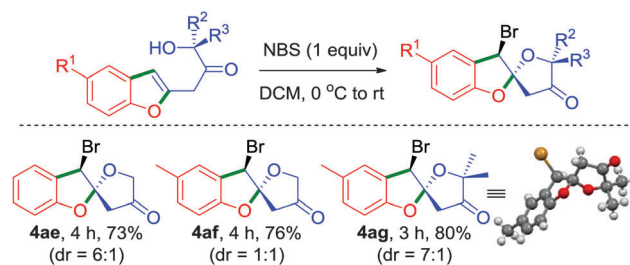
did not yield the expected 2-benzofuranyl-3-hydroxyacetones. This result has two-fold significance; it not only provided mechanistic insights into the conversion of **2** to **4**, but also provided a new entry for the synthesis of pyrano[3,2-*b*]benzofuran-3-ones.¹²

Apart from phenols, strikingly, enol such as 4-hydroxycoumarin **3i** also proved to be a distinctive reactive partner in producing furocoumarins **4ab**–**4ad** in one simple step from 6-acetoxy- β -pyrones, Scheme 2. Furocoumarins are part of several bioactive natural products and medicinally interesting compounds.¹³ Most of the synthetic approaches have focused on the construction of coumestans. Only a few methods have been described for the synthesis of furo[3,2-*c*]coumarins.¹⁴ In this regard, our approach depicted herein provides an unprecedented access for the synthesis of 2-alkylated furo[3,2-*c*]coumarins.

Based on the experimental observations, a plausible mechanism has been proposed in Scheme 3.¹⁵ The cascade process



Scheme 3 Plausible mechanism.



Scheme 4 An unusual two-step synthetic approach for spiro[benzofuran-2,2'-furan]-4'-ones from β -pyrones.

begins with an acid catalysed transacetalisation⁶ followed by an unusual Fries-type O \rightarrow C rearrangement¹⁶ which leads to the formation of a neutral but unstable intermediate **6a** in a highly regio- and chemoselective manner.¹⁷ Subsequently, **6a** undergoes aromatisation and concomitant oxa-Michael addition to form intermediate **4a'**. Furthermore, acid-induced ring-opening aromatisation of **4a'** affords the 2-benzofuranyl-3-hydroxyacetone **4a**.

To further illustrate the generality and synthetic utility of this methodology, we considered an elaboration, Scheme 4. We intended to exploit the presence of alcohol functionality in the side chain in an intramolecular haloetherification reaction which would potentially generate spiro[benzofuran-2,2'-furan]-4'-ones.¹⁸ Accordingly, reaction of the keto-alcohols **4a**, **4b** and **4l** with NBS at room temperature conveniently furnished the respective 5,5-spiroketal **4ae**–**4ag** in excellent yields, thereby establishing a mere two-step unprecedented access from readily accessible 6-acetoxy- β -pyrones. The relative stereochemistry of **4ae**–**4ag** was assigned based on the X-ray crystal analysis of **4ag**.¹⁹ Prevalence of several bioactive natural products possessing the 5,5-spiroketal scaffold renders this an attractive strategy for their easy synthesis, Scheme 4.²⁰

Finally, scalability and practicality of the cascade process were verified by conducting gram scale reactions of **2a**.⁸

In conclusion, we have described a cascade event of β -pyrones and phenols, originating out of serendipity, leading to the synthesis of 2-benzofuranyl-3-hydroxyacetones. The versatility of this strategy lies in its ability to establish unprecedented access for medicinally significant scaffolds such as 4,4a-dihydropyrano[3,2-*b*]benzofuran-3-ones, furo[3,2-*c*]coumarins, and spiro[benzofuran-2,2'-furan]-4'-ones in a short and efficient manner. Efforts to extend these methods for the total synthesis of natural products are in progress and will be communicated in due course.

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